TÍTOL: Production of Magnetite Thin Film over Steel Substrate using Hot Alkaline Nitrate Blackening Method

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Magnetite thin film obtained from the hot alkaline nitrate blackening method has been utilized for the protection of steel substrate since the 1900s. Even though this conversion coating process has been around for decades, its application is still limited to corrosion resistance in the firearms and the fasteners industry. Furthermore, there is a lack of literature that systematically analyse the effect of the parameters involved in the blackening process. For this reason, this study aims to investigate the effect of varying the blackening bath’s nitrate concentration, temperature and dwell time on the properties of the magnetite coating, especially that of wear resistance. In order to produce the magnetite coating, mild steel specimens were placed in a boiling solution made up of sodium hydroxide and sodium nitrate dissolved in water. The blackened specimens were then characterised using a battery of test; microstructure and composition analysis using a reflecting microscope and a scanning electron microscope, pin-on-disk test to analyse the wear resistance and tribological properties and corrosion resistance test using potentiodynamic polarization scanning. Consequently, it was found that the magnetite coating improves the wear resistance and corrosion properties of the steel substrate. In addition, the best magnetite coating is obtained using a blackening bath with a nitrate concentration between 25 % and 50 %, at a temperature of 140 °C and with a dwell time between 15 minutes and 30 minutes.

**Keywords (10 maximum):**

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<th>Magnetite</th>
<th>Thin film</th>
<th>Steel substrate</th>
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1. INTRODUCTION

Blackening or bluing is an electrochemical conversion coating where the iron on the surface of the substrate is oxidized into black magnetite (Fe₃O₄). This produces a black oxide thin film, which when impregnated with oil, provides protection against corrosion. In addition, the thin film also provides resistance against wear due to its hardness and its lubricating property. These properties endear it to application in the fire-arm industry and in the fasteners industry [1], as can be seen in Fig. 1.1.

![Application of the blackening process in the industry](attachment:image1.png)

**Fig. 1.1 Application of the blackening process in the industry (a) Blackened firearms (b) Blackened spur gear (c) Blackened fasteners**

There are two types of blackening or bluing process commercially used: (a) the hot blackening process and (b) the cold blackening process. The principal method used in the industry to obtain a magnetite coating is through the hot blackening process. In this process, the steel parts to be treated is immersed in a boiling solution of sodium hydroxide and sodium nitrate dissolved in water, as shown in Fig. 1.2 [2]. The blackening solution utilized in the industry is often a proprietary blend of different concentrations of the aforementioned ingredients with the incorporation of several rectifying and wetting agents that improves the efficiency of the process. In order to obtain a satisfactory coating, the parts to be blackened should be cleaned with acid to remove rust and should be soaked in hot alkaline bath to remove grease. The magnetite coating produced by the process, upon sealing with supplemental oil, can withstand up to 96 hours in the salt spray test per ASTM Specification B 117 [2].

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Unlike the hot blackening process, the black oxide coating produced by the cold blackening is not made up of magnetite. Instead the black finish produced comes from the deposition of selenium copper iron compound from the blackening solution applied to the steel substrate. Generally, the cold blackening solution, as shown in Fig. 1.3, is made up of selenium oxide and copper compounds dissolved in aqueous phosphoric acid. In addition, the cold blackening method, as implied by its name, does not involve any heating to produce the black oxide coating. The cold bluing process is typically used in the firearms restoration business to retouch the black oxide coating of vintage guns. As the black finish produced by the cold blackening solution is mainly cosmetic, the corrosion resistance and wear resistance provided by the magnetite coating produced in hot blackening process is not found in cold bluing.

There are many advantages that the blackening process offers over other types of coating. For example, the blackening process produces an attractive black finish that enhances the saleability of the coated articles. In addition, the process also offers an economical means of imparting moderate corrosion resistance and wear resistance to the treated parts. Furthermore, the magnetite coating produced caused very little dimensional change to the steel parts, which is vital for moving parts.

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4 http://www.pfonline.com/articles/aiming-for-the-perfect-finish
5 www.midwayusa.com
With regards to the process itself, it is fairly simple and very flexible, such that a great variety of steel alloys can be blackened by using the same procedure. Moreover, contrary to other conversion coating and electroplating processes which requires extensive pre-cleaning of the parts, inadequate cleaning of the parts is not a problem for the hot blackening process. This is due to the high alkalinity of the blackening solution and the slight agitation due to boiling action in the blackening bath. Besides, the environmental effect of the blackening process is less grave than other electrochemical and conversion coating processes. The chemicals used in the blackening bath is not toxic like the chromate ions used in chromate conversion or cyanides used in electroplating baths. In most cases, neutralization of the alkaline solution is all that is required to nullify the environmental effects.

Although the hot alkaline nitrate blackening process has been around since the 1930s, the application of the blackening process has been limited to providing corrosion resistance to steel parts. In addition to corrosion properties, it is known that the magnetite coating produces through the blackening process possesses some lubricating property [2], which can be beneficial for industries dealing with mobile steel parts. For example, the lubricating effect and wear-resistance of magnetite thin film can be of assistant to thermal spray deposited iron-based coating which experience problems of wear due to oxidation and deformation of steel splats [3]. The steel-based coating, in turn, is projected to aluminium parts used in the automotive industry in order to provide wear-resistance to the parts.

This work is aimed to investigate the parameters involved in the hot alkaline blackening process and their effect on the mechanical and chemical properties of the blackened specimens. The nitrate concentration of the blackening bath, the bath temperature and the dwell time of bare mild steel specimens in the blackening bath were manipulated in this study and the properties of the magnetite coating obtained were analysed. Analysis of the blackened specimens were carried out to determine the magnetite coating thickness, surface microstructure, microhardness, friction characteristic, wear resistance and electrochemical corrosion resistance.
1.1. Previous researches


R. M. Hurd and N. Hackerman (1957) of the University of Texas studied the reaction kinetics of the formation of magnetite coatings on mild steel in hot alkaline nitrite solution. In the study, mild steel specimens were immersed in concentrated solutions of sodium hydroxide and sodium nitrite heated within a temperature range of 130 °C - 150 °C. The change in the mass of the specimens over time were recorded and analysed to determine the reaction rate.

As a result of the experiments, it was found that the iron atoms on the surface of the steel were dissolved into the solution over time. Of the iron that is dissolved into the solution, only 30% was precipitated on the surface of the steel as magnetite. Furthermore, as the magnetite coating grows on the steel surface, the reaction rate was found to have dropped to a fraction of the initial reaction rate. This observation is explained by the fact that as the magnetite coating thickens, the diffusion of the reactants through the magnetite layer to the steel surface reduces, thus reducing the reaction rate.

The following mechanism was proposed to explain the findings:

\[ Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+ \quad (1.1.1.1) \]
\[ Fe(OH)_2 + H_2O \rightleftharpoons Fe(OH)_3 + H^+ + e^- \rightleftharpoons FeO_2^- \quad (1.1.1.2) \]
\[ Fe^{2+} + 2FeO_2^- \rightarrow Fe_3O_4 \quad (1.1.1.3) \]

1.1.2. The protection effectiveness of magnetite layers in relation to boiler corrosion [5]

W.M.M. Huijbregts and A. Snel (1972) presented a paper on the effectiveness of magnetite layers in protecting the surface of a steel boiler from corrosion at the 5th International Congress on Metallic Corrosion, Tokio. In this paper, several steel samples of different compositions were immersed in sodium hydroxide, NaOH solution at 300 °C for 30 - 45 days. The concentration of sodium hydroxide in the solution was varied to see the effect of pH on the formation of magnetite coating.

The weight of the specimens were recorded after being taken out from the sodium hydroxide solution and again after being reduced in hydrogen atmosphere. The weight gain of the specimens were determined by finding the difference in weight before and after the hydrogen reduction. In addition, the oxidation rate of the specimens over time were determined from the weight gain data obtained over time.

The result of the study was that the oxidation rate of the specimens follows a logarithmic pattern with increasing time in the solution. Thus, this observation shows that the longer the specimens were in the solution, more pores on the magnetite layers are blocked due to the growth of magnetite grains on the specimens’ surface.
1.1.3. The mechanism of high temperature aqueous corrosion of steel [6]

J. Robertson (1989) investigated the mechanism of the formation of magnetite layers on mild steel in high temperature aqueous solutions. The pH and the temperature of the solutions were varied in the investigation and the resulting mass difference of the mild steel specimens were recorded. In addition, the morphology and the microstructure of the obtained magnetite layers were observed using a scanning electron microscope.

The specimens obtained in the study demonstrates the presence of duplex layers of magnetite on the steel surface. These duplex layers consist of an inner magnetite layer and an outer magnetite layer. The inner magnetite layer is composed of a small-grain, low-porosity crystal structure, while the outer magnetite layer consists of larger crystallites with higher porosity.

As a result, this study suggests that the magnetite coating grows on two fronts by two different mechanisms. On one hand, the magnetite coating grows outwards from the steel-magnetite interface via the direct oxidation mechanism, thus forming the inner magnetite layer. In the direct oxidation mechanism, water diffuses into the steel-magnetite interface through micropores in the magnetite and reacts with the steel to form more magnetite. On the other hand, the outer magnetite layer is formed by the precipitation mechanism, where magnetite particles are deposited from the solution-magnetite interface. The precipitation mechanism is governed by the diffusion of iron, Fe ions from the steel outwards into the solution via the magnetite grain boundaries.

The two mechanisms of magnetite formation are described below:

- Direct oxidation mechanism

\[
Fe + 2H_2O \rightleftharpoons HFeO_2^- + 3H^+ + 2e^- \quad (1.1.3.1)
\]

\[
3HFeO_2^- + H^+ \rightarrow Fe_3O_4 + 2H_2O + 2e^- \quad (1.1.3.2)
\]

- Precipitation mechanism

\[
3Fe(OH)_2 \rightleftharpoons Fe_3O_4 + 2H_2O + H_2 \quad (1.1.3.3)
\]

H. Zhu, F. Cao, D. Zuo et al. (2007) proposed a novel technology to blacken the surface of carbon steel. In this technology, a black coating composed of magnetite, Fe$_3$O$_4$ particles were deposited onto the steel surface via hydrothermal treatment of the steel substrate.

The hydrothermal treatment was carried out in a solution composed of sodium hydroxide, NaOH, iron (II) sulphate, FeSO$_4$, and hydrazine, N$_2$H$_4$ heated to a temperature of 150 °C for 8 hours. The magnetite coatings obtained were then characterised with a field emission scanning electron microscope (FESEM) to observe their microstructure. The composition of the samples obtained were also determined using an X-ray diffractometer. In addition, the bare steel sample and the blackened samples were also subjected to electrochemical analysis to determine their corrosion resistance.

Through the experiments, it was found that the magnetite coating obtained has a thickness of around 3 μm and the presence of the coating improves the corrosion resistance of the steel substrate. The result of the electrochemical analysis shows that the specimen with the magnetite coating has a corrosion potential of -0.4 V and a corrosion current density of 0.001 A/cm$^2$ in the anodic branch, whereas the bare steel specimen has a lower corrosion potential (-0.55 V) and a higher corrosion current density in the anodic branch (0.1 A/cm$^2$).

Furthermore, it was observed in the experiment that the ferromagnetism of the steel substrate plays an important role in attracting the magnetite particles in the solution to the steel. As the magnetite particles become concentrated near the surface of the steel, the particles precipitates out of the solution to the steel surface.

A three-stage mechanism was proposed for the formation of the magnetite coating in this blackening technology. The first stage of the mechanism consists of the oxidation of the iron atoms on the surface of the steel sample, which consequently produces a thin discontinuous magnetite film. Later, in the second stage, magnetite nanoparticles was formed in the solution via the reaction between the iron (II) sulphate, FeSO$_4$, and the sodium hydroxide, NaOH, in presence of hydrazine, N$_2$H$_4$. Finally, the magnetite nanoparticles were hydrothermally deposited onto the discontinuous magnetite film to form dense magnetite coating.
1.1.5. Features of Formation of Magnetite Coatings on Low–Carbon Steel in Hot Nitrate Solutions [8]

Yu. I. Kuznetsov, D. B. Vershok, S. F. Timashev et al. (2010) examined the mechanism of the formation of magnetite coatings on low-carbon steel in alkali-free nitrate solutions at the temperatures of 70 – 98 °C. In the study, steel specimens were immersed in an ammonium nitrate, NH\textsubscript{4}NO\textsubscript{3} solution with GAMC-5 additive and the electrochemical behaviour of the low carbon steel were observed over time.

The pH, the free corrosion potential and the corrosion current of the steel specimens were recorded over time and analysed to determine the mechanism of magnetite formation. In addition, the evolution of the thickness and the microstructure of the magnetite coating over time were also observed using an atomic force microscope (AFM).

Three possible mechanisms of magnetite formation were proposed in the paper; two involving the dissolution of the iron atoms from the steel surface and one involving the direct oxidation of the iron atoms on the steel surface. The first mechanism, as shown below, involves the dissolution of iron atoms into iron (II) ions, Fe\textsuperscript{2+}, which later reacts with water to form iron (II) hydroxide, Fe(OH)\textsubscript{2}. The iron (II) hydroxide then undergoes a reversible reaction to form magnetite particles, Fe\textsubscript{3}O\textsubscript{4}, which are later deposited onto the specimen’s surface.

\[
Fe \rightarrow Fe^{2+} + 2e^- \quad (1.1.5.1)
\]
\[
Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+ \quad (1.1.5.2)
\]
\[
3Fe(OH)_2 \rightleftharpoons Fe_3O_4 + 2H_2O + H_2 \quad (1.1.5.3)
\]

Another mechanism, shown below, suggests that the iron (II) hydroxide is later partially oxidised into iron (III) hydroxide, Fe(OH)\textsubscript{3}. The iron (III) hydroxide ion undergoes a reversible reaction to form iron (III) oxide ion. The iron (III) oxide ion and the iron (II) hydroxide ion then undergo a condensation reaction to form magnetite, Fe\textsubscript{3}O\textsubscript{4} spinel which is then precipitated on the substrate’s surface.

\[
Fe(OH)_2 + H_2O \rightleftharpoons Fe(OH)_3 + H^+ + e^- \quad (1.1.5.4)
\]
\[
Fe^{2+} + 2FeO_2^- \rightarrow Fe_3O_4 \quad (1.1.5.5)
\]

In the presence of nitrate ion, which acts as the oxidising agent, iron on the surface of the substrate can be oxidised directly into magnetite while the nitrate ion is reduced into ammonium hydroxide, NH\textsubscript{4}OH. This is the third mechanism, which is demonstrated in the following equations.

\[
3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 8H^+ + 8e^- \quad (1.1.5.1)
\]
\[ NO_3^- + 7H_2O + 8 e^- \rightarrow NH_4OH + 9 OH^- \] (1.1.5.1)

As a result of the analysis done in the experiments, it was perceived that the pH near the specimen’s surface increases soon after the immersion of the steel specimen. This proves that the iron atoms were dissolved into the solution, forming alkaline iron hydroxides. Moreover, the corrosion current was found to increase for a period of 10 minutes and then decreases for a longer time period. This shows that the iron ions gradually saturates the solution for 10 minutes before the iron ions were transformed into magnetite and precipitated onto the specimen’s surface. In addition, the decrease in the corrosion current after reaching a maximum shows that as the magnetite coating thickens, the steel surface is blocked by the magnetite, minimising the dissolution of the iron atoms on the steel surface. Furthermore, magnetite nuclei were detected in the early stages of the magnetite coating formation, confirming the presence of direct oxidation of the steel surface.

1.1.6. Tribological properties of magnetite precipitate from oxide scale in hot-rolled micro alloyed steel [9]

X. Yu, Z. Jiang, D. Wei et al. (2013) examined the tribological properties of magnetite precipitate from oxide scale in hot-rolled micro alloyed steel in this paper published in volume 302 of Elsevier’s Wear journal. Low carbon microalloyed steel specimens were oxidised at 800 °C for 120 seconds in 19.5 % humid air in the study in order to simulate the hot-rolling process of plain steel. The specimens were then held at 550 °C for 60 - 300 minutes in argon seal in order for the magnetite to precipitate out of the oxide scale.

The obtained specimens were subjected under the pin-on-disk test to study their friction and wear rate properties. Afterwards, the composition and the microstructure of the specimens were characterised using a scanning electron microscope (SEM) in conjunction with energy dispersive X-ray spectroscopy (EDS).

The study managed to find out that the oxidation of the steel specimens produces two types of magnetite precipitates; a globular magnetite structure and a lamellar magnetite structure. The globular magnetite structure was formed after 60 minutes holding time at 550 °C, whereas the lamellar magnetite structure was formed after 120 minutes. The globular magnetite structure was found to have a low coefficient of friction and a low wear rate, consequently it could serve as a lubricant and a wear resistant coating over the steel. On the contrary, the lamellar magnetite structure has a higher coefficient of friction and experiences some adhesion wear.

Furthermore, the coefficient of friction of the magnetite precipitate found in the study ranges between 0.40 and 0.56. The coefficient of friction was also found to decrease with increasing sliding speed.
2. EXPERIMENTAL PROCEDURES

Low-carbon AISI 1117 steel rectangular plates, with compositions and properties shown in Table 1, were used in the blackening experiments. The specimens were prepared using a Struers Labotom-3 cut-off machine with coolant, as shown in Fig. 2.1. The coolant is important in order to preserve the microstructure of the specimens, which could be altered by the heat generated during the cutting. The plates were cut into specimens of two sizes; a smaller piece for microscopic analysis and a bigger piece for hardness test, tribological test and corrosion test.

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Hardness (HV)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Fe (%)</td>
<td>C (%)</td>
</tr>
<tr>
<td>AISI 1117 steel</td>
<td>98.67</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table 1 The chemical composition and hardness of the steel specimen

In continuation, the specimens were treated in 35 % hydrochloric acid, HCl solution in order to remove any rust on the surface of the specimen. After the acid treatment, the specimens were then mounted in black MultiFast® resin in a Struers LabPress-3 hot mounting press, as demonstrated in Fig. 2.2. The specimens were mounted with their wide face up under a force of 20 kN at a temperature of 150 °C for 3 minutes. In addition, the cooling time is set at a low value of 1 minutes so that the resin is brittle and easily broken. This is because the resin must be broken off the specimens after they are polished to a mirror finish in order to be later blackened.
Next, the mounted specimens were then polished to a mirror finish using #180 SiC grinding paper, #800 SiC grinding paper and 1 μm alumina suspension. As seen in Fig. 2.3, a Struers RotoPol-11 automatic grinding machine running is used to polish the mounted specimens. The specimens were polished under a force of 30 kN, which is provided by compressed air. Moreover, the specimens were polished at a speed of 150 rpm for 5 minutes per grinding paper.

The resin was later broken off using an engineer’s vice, leaving behind the polished specimens. Next, the prepared specimens were weighed using an electronic balance and put into a blackening bath at a certain temperature and for a certain dwell time. As seen in Fig. 2.4, the blackening experiments were carried out in a fume chamber in order to contain the noxious fumes and the corrosive contents.
of the bath. After that, the blackened specimens were taken out of the bath, rinsed in cold water, dried and weighed.

The hot alkaline bath used in the blackening process consists of sodium hydroxide, NaOH, sodium nitrate, NaNO₃ and distilled water, as shown in Fig. 2.5. The solution was made by first dissolving sodium nitrate powder in distilled water and then heating the solution to a boil. The sodium hydroxide pellets were then put into the solution little by little until the desired boiling temperature is achieved.

Different bath compositions were used to investigate the effect of the concentration of sodium nitrate and sodium hydroxide to the quality of the magnetite coating. Four batches of blackening bath were made; a 10 % nitrate bath, a 25 % nitrate bath, a 50 % nitrate bath and a 100 % nitrate bath.
Adding sodium hydroxide pellets into the blackening bath or boiling off the water from the solution increases the boiling temperature of the solution due to the colligative properties of water. Using this fact, the specimens were blackened at 130°C, 140°C and 150°C to study the influence of temperature on the coating.

Fig. 2.6 shows the setup used in the blackening experiments, where the blackening solution in the conical flask was heated using an electric heater. The heater was put at the highest power setting so as to bring the solution to a boil. The blackening bath has to be brought to a boil in order for the oxidation reaction to take course. A thermometer dipped in the blackening bath was used to monitor the boiling temperature of the bath. In addition, the tap situated above the conical flask adds water to the solution to replace water loss in the solution due to evaporation while controlling the bath temperature.

Upon the attainment of the desired bath temperature, three pairs of specimens were dropped into the blackening bath to be blackened. A pair is taken out every 15 minutes in order to vary the dwell time of the specimens in the bath. Consequently, for each experiment, three pairs of specimens blackened for 15, 30 and 45 minutes were obtained.
As a result of the blackening bath, the specimen’s colour turns from grey to black, as shown in Fig. 2.7. It can also be observed that the surface finish of the blackened specimens mirrors that of the steel specimens.

The rectangular mild steel specimens used in the experiment: (a) before blackening (b) after blackening

The experimental procedures described beforehand can be summarised in Fig. 2.8. It can be seen that the rectangular steel plate was cut laterally in the cut-off machine in Fig. 2.8 (a). The cut specimens were later treated in hydrochloric acid (b), mounted in resin (c), and polished to a mirror finish (d). The specimens were then broken off the resin and dropped into the blackening bath (e). After a certain dwell period, the specimens were then immersed in tap water and dried (f).
Fig. 2.8 The experimental procedures: (a) specimen cutting (b) acid pickling (c) specimen mounting (d) grinding process (e) specimen blackening (f) immersion in cold water
3. SPECIMEN CHARACTERIZATION

In order to perform tests and analyse the blackened specimens, they were mounted in either MultiFast® or PolyFast® resins in function of the analysis to be done. The smaller specimens were mounted on black Polyfast® resin, as shown in Fig. 3.1, since they were destined for microstructure and thickness analysis. The Polyfast® resin was used due to its good edge retention and good electrical conductivity which makes it suitable for scanning electron microscope (SEM) analysis. The mounting process is carried out under 20 kN load, at 150 °C and for 6 minutes, with a cooling time of 3 minutes. On the contrary, the cheaper MultiFast® resin is used to mount the larger specimens used for the hardness test and the pin-on-disk test.

![Image of PolyFast® resin and MultiFast® resin](image)

**Fig. 3.1** The hot mounting resins used and the mounted specimens: (a) The PolyFast® resin used to mount the transversal specimen for microstructure analysis (b) The MultiFast® resin used to mount the specimen for the surface analysis.

The microstructure and thickness of the magnetite thin-film was studied using a reflecting microscope (LEICA IM-1000), as seen in Fig. 3.2. Before the specimens were characterised, the specimens mounted in the Polyfast® resin were polished using #180, #500, #800, #1200 SiC grinding paper and 1 μm alumina colloidal suspension. The polishing process was carried out under 20 kN force, at 150 rpm and for 5 minutes for each grinding paper grade.
After the specimens had been polished, the specimens were placed upside down on the viewing platform of the microscope. The specimens were observed under an augment of 2.5 x 1.0 initially, gradually increasing the augment until the magnetite coating can be detected. Most of the time, the magnetite coating can be clearly discerned at an augment of 50 x 1.0. The specimens were examined under moderate light intensity and without any colour or polarisation filters. Furthermore, the micrograph of the specimens were captured using the QWIN© software which comes with the microscope.

Next, a SEM (JEOL JSEM-5600) was utilized to further characterise the microstructure of the specimens, as shown in Fig. 3.3. The short wavelength of the electron beam used in the SEM makes it possible to obtain higher resolution micrographs of the specimens. There are three signals that can be captured by the SEM; back-scattered electrons (BSE), secondary electron (SE) and characteristic X-ray spectrum. The best micrographs of the specimens were obtained from the secondary electron image at 20 kV intensity and at a magnification of 1500 x.

**Fig. 3.2** The Leica IM 1000 light microscope used to analyse the microstructure of the specimen

**Fig. 3.3** The JEOL JSEM-5600 scanning electron microscope (SEM) used to characterise the magnetite coating
In addition, the chemical composition of the magnetite coating and the underlying steel substrate was examined using energy dispersive X-ray spectroscopy (EDS). The EDS spectrum is analysed using the INCA® software, which plots the X-ray peaks corresponding to the elements in the specimen. In addition to knowing the elements present in the specimen, a quantitative analysis of the peaks using the software also enables the determination of the empirical formula of the magnetite coating.

Meanwhile, some of the specimens mounted in MultiFast® resin were taken to the Fisherscope microhardness testing equipment shown in Fig. 3.4 to determine their surface hardness. There, the specimens’ surface were subjected to a 100 mN load transmitted via a pyramidal-shaped Vickers indenter. The load was gradually increased from zero to 100 mN in 20 seconds, maintained at the maximum load for 5 seconds and then decreased for the same amount of time that it took for loading.

![Fisherscope microhardness testing equipment](image)

*Fig. 3.4 The Fisherscope microhardness testing equipment used to measure the hardness of the coating*

The WIN-HCU® software, which accompanies the testing equipment, monitors the penetration depth of the indenter and plots a graph of the load against the penetration depth. The resultant loading and unloading curves were then used by the program to calculate the Vickers hardness value (HV) of the surface of the specimen. Several points on the surface of each specimens were indented and the measured hardness of each point were averaged out. Besides calculating the hardness value of the specimens, the microscope which forms part of the testing equipment can be used to analyse the produced indentations on the specimens’ surface.

Afterwards, tribological tests were carried out under a pin-on-disk configuration on a CSEM tribometer as shown in Fig. 3.5. The pin used in the tests is that of a tungsten carbide (WC) ball with a diameter of 6 mm. In the pin-on-disk test, the tungsten carbide ball is dragged across the specimen rotating at a specific speed and the frictional force exerted on the pin is measured by the strain gauge located in the load arm. The coefficient of friction of the specimen is then calculated by dividing the measured frictional force with the value of the applied load.
The pin-on-disk tests were carried out on the specimens mounted on the MultiFast\textsuperscript{©} resin. The procedures to perform the test are as follows:

1. First, the mounted specimen was placed on the stage below the pin and fixed in place by the clamps on the stage.
2. Next, the radius of the wear track was adjusted using the lever located on the left hand side of the equipment.
3. The load arm of the tribometer was then levelled horizontally by screwing or unscrewing the adjustable the sample stage.
4. Finally, a 5 N load was placed on the arm over the pin holder and the test is launched using the TRIBOMTR\textsuperscript{©} software. Using the software, the test was performed at a speed of 5 cm/s and for 5000 revolutions.
5. In order to maintain the reliability of the friction measurements, the revolution speed and the frictional force were calibrated at least once a week.

The wear track generated by the tungsten carbide ball in the pin-on-disk test was then analysed using a Form TalySurf\textsuperscript{©} surface profiler, as shown in Fig. 3.6. The surface profiler analyses the surface of the specimen by using a diamond stylus that is moved laterally across the specimen. The vertical displacement of the diamond stylus as it moves across the specimen generates an analog signal, which is then converted into a digital signal and displayed by the software Talyprofile\textsuperscript{©} that comes with the profiler.
In order to determine the wear resistance of the specimen, the volume of the wear track, $W$, of the specimen was first calculated by multiplying the wear track area, $A$, obtained by the surface profiler with the circumference of the wear track. The circumference of the wear track is obtained by multiplying the radius, $R$, with $2\pi$:

$$W = A \cdot 2\pi R \text{ mm}^3$$  \hspace{1cm} (3.1)

Next, the volume of the wear track, $W$, was then divided with the sliding distance, $L$, to yield the wear rate experienced by the specimen. The sliding distance, in turn, is obtained by multiplying the circumference of the wear track with the number of revolutions, $N$:

$$w = \frac{W}{L} = \frac{W}{N \cdot 2\pi R} \text{ mm}^3/m$$  \hspace{1cm} (3.2)

After the wear rate has been calculated, the specific wear rate, $w_s$, which determines the intrinsic wear resistance of the specimen, is calculated by dividing the wear rate with the load, $P$:

$$w_s = \frac{w}{P} \text{ mm}^3/m \cdot N$$  \hspace{1cm} (3.3)
Finally, the corrosion resistance of the specimens was determined using the potentiodynamic polarization test. The test was carried out using a VersaSTAT 4 potentiostat as seen in Fig. 3.7 (a). In order to simulate a coastal environment, a 3.5 % sodium chloride, NaCl solution was used as the electrolyte in the electrochemical cell. As shown in Fig. 3.7 (b), a three electrodes configuration was utilized in the tests; a platinum electrode, a saturated calomel electrode (SCE) and the specimen’s surface connected to the ground. All potentials were measured with respect to the SCE (0.244 V versus SHE) as the reference electrode.

Before the potentiodynamic polarisation scan was started, the open-circuit potential (OCP) was first measured for approximately one hour. As can be observed in Fig. 3.8, a cyclic voltammetry technique was chosen to perform the scan. In this technique, the potential applied between the SCE and the titanium electrode is increased up to a maximum potential and then decreased back to the starting potential. The scan was started at the OCP and the potential was increased at a rate of 2.0 mV/s until a maximum potential of 1.5 V and then decreased to -0.6 V.
After one hour of the OCP measurement, the potentiodynamic scan was carried out for around another 45 minutes. During the course of the test, the surface of the specimen undergoes oxidation, thus it acts as the anode in the test. As the specimen potential is scanned slowly in the positive going direction, the resultant current is measured by an ammeter to determine the corrosion characteristic of the specimen.

In addition to the tests described above, the changes in mass of the specimens before and after the blackening bath were also recorded and analysed. The mass of the specimens were measured using an electronic balance with a precision of up to 0.001 g. In order to compensate for the variation in size and surface area of the specimens, the mass change calculated is divided with the initial mass of the specimen to obtain the relative mass change in percentage.
4. RESULTS AND ANALYSIS

In order to investigate the effect of the blackening bath nitrate concentration, temperature and the specimen’s dwell time on the magnetite coating, a series of tests were run on the specimens. The specimens’ mass change during the blackening process as well as the microstructure of each specimen were documented and analysed. In addition, the specimens were also subjected to microhardness test, pin-on-disk test and corrosion test.

4.1. Mass change

The percent mass difference between the specimen before and after the blackening process were recorded and its variation with the dwell time and blackening temperature is shown in Fig. 4.1.1. It can be seen that the specimens lose mass after they are blackened. The possible reason behind the loss in mass is that some of the heavier iron atoms are lost in the bath solution and substituted with lighter oxygen atoms which reacts with iron to form magnetite, Fe₃O₄.

![Graph of the change in percent mass difference of the specimens with the dwell time and the temperature of the 10% nitrate blackening bath.](image-url)
Furthermore, it can be seen in Fig. 4.1.1 that, for a given bath temperature, the loss in mass of the specimens generally increases with increasing dwell time up to 30 minutes, upon which the specimen starts gaining mass. This observation can be explained by the fact that the iron atoms on the surface of the specimens were dissolved into the solution by the concentrated sodium hydroxide in the solution, hence the specimens lose mass during the first 30 minutes. Afterwards, due to the growth of the magnetite coating and the subsequent closing of the pores on the magnetite coating, the reactants in the solution could not diffuse into the steel surface and the iron atoms could not diffuse out into the solution. Consequently, the specimens stop losing mass from the dissolution of iron atoms into the solution.

The effect of the temperature of the blackening bath can also be observed in Fig. 4.1.1. As the bath temperature increases, the specimen loses more mass in the blackening bath since the oxidation reaction rate increases with increasing bath temperature. Hence, it can be seen that the least mass loss is noted for the specimen blackened at a temperature of 130 °C for 15 minutes, while the greatest mass loss is experienced by the specimen blackened at 150 °C for 45 minutes.

Meanwhile, an opposite trend in mass change is obtained for the specimens blackened in the 25 % nitrate blackening bath. As seen in Fig. 4.1.2, the greatest loss in mass is experienced by the specimen blackened at a temperature of 130 °C for 15 minutes, while the least mass loss is experienced by the specimen blackened at 140 °C for 15 minutes.

Fig. 4.1.2 Graph of the change in percent mass difference of the specimens with the dwell time and the temperature of the 25 % nitrate blackening bath.
Besides, the specimens blackened in the 25 % nitrate bath seem to generally lose more mass the longer they sit in the blackening bath. This is with the exception of the specimens blackened at 130 °C, which gain more mass the longer they sit in the blackening bath. The combined effect of the lower concentration of sodium hydroxide in the blackening bath and the low bath temperature could explain the mass gain experienced by the specimens blackened at 130 °C. At low bath temperature and low pH, the removal of the iron atoms off the specimen’s surface occur much slowly compared to the growth of the magnetite coating, thus causing a net increase in mass of the specimens.

Fig. 4.1.3 shows the mass loss in the specimens blackened in the 50 % nitrate blackening bath. The mass loss is seen to increase with increasing bath temperature similar to the specimen blackened in the 10 % nitrate bath. The specimens blackened at 130 °C lost an average of 0.2 % of their initial mass, while the specimens blackened at 140 °C and 150 °C lost an average of 0.35 % and 0.57 % of their initial mass, respectively.

\[ \text{Fig. 4.1.3 Graph of the change in percent mass difference of the specimens with the dwell time and the temperature of the 50} \% \text{ nitrate blackening bath.} \]

In addition, it is worth noting that the amount of mass loss at different dwell times was approximately constant for a given bath temperature and nitrate concentration. Thus, it can be deduced that the oxidation of the steel specimens blackened in the 50 % nitrate bath occurred shortly upon their introduction in the blackening bath and was finished before 15 minutes.
The specimens blackened in the 100 % nitrate bath experience the least loss in mass compared to the other specimens, as can be observed in Fig. 4.1.4. Moreover, it can be seen that, with the exception of the specimens blackened at 150 °C, the amount of mass loss at different dwell times was approximately constant for a given bath temperature and nitrate concentration. This observation is similar to that of the specimens blackened in the 50 % nitrate bath. The specimen blackened at 150 °C gains mass with increasing dwell time up to 30 minutes, upon which it began to lose mass. The reason behind this phenomenon is that during the first 30 minutes, magnetite particles already present in the solution from previous blackening were precipitated onto the steel specimen. Due to the porous nature of the magnetite coating produced by the precipitation mechanism, sodium hydroxide from the solution can pass through the magnetite coating to the underlying steel substrate and dissolve the iron atoms. As a consequence, the specimens loses mass at dwell times superior to 30 minutes.

In addition, the mass loss in the specimens blackened at 130 °C and 140 °C is practically similar to each other, as can be seen in Fig. 4.1.4. The mass loss at 150 °C, however, is much greater than the specimens blackened at lower temperatures. The possible reason behind this sudden jump in mass loss is that the combined effect of the higher pH value and the higher temperature of the blackening bath causes a greater amount of the iron atoms on the steel surface to be dissolve into the blackening solution, provoking a greater mass loss.

To summarise, the specimens typically lose mass during the initial period of blackening due to the dissolution of the iron atoms on the steel surface. As the magnetite coating grows, the pores on the magnetite coating are blocked, inhibiting further mass loss by the dissolution of iron atoms.
Furthermore, different bath temperatures and nitrate concentrations also play important roles in dictating the oxidation rate of the steel specimens. As can be seen in Fig. 4.1.5, the specimens loses more mass at higher bath temperature, the exception being that of the specimens blackened in the 25 % nitrate bath. With regards to the nitrate concentration, the specimens blackened in the 25 % nitrate bath loses the most mass, while the least mass is lost for the specimens blackened in the 100 % nitrate bath.

Fig. 4.1.5 Graph of the change in percent mass difference of the specimens with the temperature of the blackening bath and the nitrate concentration.
4.2. Microstructure analysis

Magnetite coating is a conversion coating produced through the oxidation of the iron atoms on the steel surface. For this reason, the microstructure of the magnetite coating follows that of the underlying steel surface. Fig. 4.2.1 demonstrates this fact by showing the magnetite grains on the surface of the coating.

![Figure 4.2.1](image1.png)

Fig. 4.2.1 Micrographs of the surface of the magnetite coating: (a) reflecting microscope, (b) SEM

The cross-section of the magnetite coating were observed by a reflecting microscope and a SEM and their micrographs are shown in Fig. 4.2.2. The grey layer between the black resin and the white steel is the magnetite layer. As is observed in the micrographs, the magnetite layer is continuous and quite uniform in thickness.

![Figure 4.2.2](image2.png)

Fig. 4.2.2 Micrographs of the thickness of the magnetite coating: (a) reflecting microscope, (b) SEM
In order to confirm the chemical composition of the grey layer observed in the micrographs, an energy dispersive X-ray spectrometry (EDS) spectrum of the layer was analysed. Fig. 4.2.3 shows the EDS spectrum of the grey layer, where iron and oxygen peaks can be observed in the spectrum. This observation proves the presence of magnetite in the layer. Further numerical analysis of the spectrum of the layer shows that it consists of 58.62 % oxygen atoms and 41.38 % iron atoms, which corresponds with the empirical formula of magnetite, Fe₃O₄.

![Fig. 4.2.3 The EDS spectrum of the magnetite coating showing the iron and oxygen constituents](image)

The magnetite coating obtained in the experiments has an average thickness of around 3 μm and can grow up to a maximum thickness of 6 μm. The explanation behind this limiting thickness is that as the magnetite layer grows, it becomes harder for the oxygen atoms to diffuse into the underlying steel surface. As the magnetite coating reaches the limiting thickness, the oxidation reaction of the iron to form magnetite is slowed down until it stopped.
In continuation, the micrographs of the different specimens taken by a reflecting microscope are exhibited. Fig. 4.2.4 shows the cross-section of the specimens blackened in a 10% nitrate bath at different temperatures and dwell times. As can be seen in Fig. 4.2.4, the thickness of the magnetite coatings averaged out at 3.04 μm and the coatings appear dense and uniform.

![Micrographs](image)

**Fig. 4.2.4** Micrographs of the specimens blackened in the 10% sodium nitrate (NaNO₃) bath: (a) 130 °C, 15 minutes (b) 130 °C, 30 minutes (c) 130 °C, 45 minutes (d) 140 °C, 15 minutes (e) 140 °C, 30 minutes (f) 140 °C, 45 minutes (g) 150 °C, 15 minutes (h) 150 °C, 30 minutes (i) 150 °C, 45 minutes

In addition, as observed in Fig. 4.2.4, the thickness of the coating is greatest for the specimen blackened at 130 °C and for 15 minutes (4.4 μm). Meanwhile, the specimen blackened at 130 °C and for 30 minutes has the lowest average thickness among the specimens (2.1 μm).
The cross-section of the specimens blackened in a 25 % nitrate bath at different temperatures and dwell times is shown in Fig. 4.2.5. As can be seen in Fig. 4.2.5, the thickness of the magnetite coatings averaged out at 3.77 μm and the coatings appear dense and uniform.

Contrary to the specimens blackened in the 10 % nitrate bath, the magnetite coating is thickest for the specimen blackened at 140 °C and for 30 minutes (5.8 μm). The specimen with the thinnest magnetite coating (blackened at 140 °C and for 15 minutes), on the other hand, has an average thickness of 2.5 μm.
Fig. 4.2.6 shows the cross-section of the specimens blackened in a 50 % nitrate bath at different temperatures and dwell times. As can be seen in Fig., the thickness of the magnetite coatings averaged out at 3.25 μm and the coatings appear dense and uniform.

Similar to the specimens blackened in the 10 % nitrate solution, the specimen blackened at the lowest temperature and for the least amount of dwell time has the thickest magnetite coating (4.1 μm) in this case. On the contrary, the magnetite coating is thinnest (2.3 μm) for the specimen blackened at 140 °C and for 45 minutes.
Fig. 4.2.7 shows the cross-section of the specimens blackened in a 100 % nitrate bath at different temperatures and dwell times. As can be seen in Fig. 4.2.7, the thickness of the magnetite coatings averaged out at 2.21 μm and the coatings appear dense and uniform.

Furthermore, the specimens blackened in the 100 % nitrate bath has the thinnest magnetite coating compared to the specimens blackened in the other blackening solutions. For instance, the specimen blackened at 140 °C and for 45 minutes has an extremely fine coating, that the magnetite coating can’t be distinguished under the optical microscope.
A trend is observed on the variation of the thickness of the magnetite coating with the temperature of the blackening bath. This is illustrated in Fig. 4.2.8, where the coating thickness is seen to be increased with increasing bath temperature, with the exception for the 25 % nitrate bath. Consequently, the maximum thickness is obtained at a temperature of 150 °C. The reason behind this observation is that at higher bath temperature, the oxidation rate of the steel substrate into magnetite increases, hence producing a thicker magnetite coating.

![Graph of the variation of the thickness of the magnetite coating](image)

**Fig. 4.2.8** Graph of the variation of the thickness of the magnetite coating with the dwell time and the nitrate concentration of the blackening bath, with the bath temperature maintained at 140 °C.

Furthermore, it can also be observed in Fig. 4.2.8 that the coating thickness is greatest at a nitrate concentration of 25 %, followed by 50 %, 10 % and 100 %. The reason behind this tendency is that at low concentration of NaNO₃, the NaOH concentration in the blackening bath is correspondingly higher. The high pH value consequently provokes the dissolution of the magnetite coating, causing the coating thickness to be reduced. In contrast, at high concentration of NaNO₃, the salt in the blackening bath is precipitated out of the solution. The precipitated salt then cover up the surface of the specimens thus inhibiting the oxidation of the specimens.
The effect of the precipitated salt on the blackening of the specimen can be observed in Fig. 4.2.9. A rich iridescent surface, as seen in Fig. 4.2.9, is obtained for the specimens blackened in the 100 % nitrate bath.

Fig. 4.2.9 The iridescent surface of the specimen blackened in the 100 % nitrate bath at 150 °C for 10 minutes: (a) visual inspection (b) at an augment of 100X
4.3. Vickers indentation hardness test

The specimens were indented using Vickers pyramidal shaped indenter in order to figure out their surface hardness, as observed in Fig. 4.3.1. A maximum load of 100 mN is applied by the indenter on the surface of the specimens and the penetration of the indenter was monitored upon the loading and unloading stage. The surface hardness of the specimens were then calculated from the resultant penetration against load curves.

![Indentation produced by the Vickers pyramidal indenter on: (a) steel (b) blackened steel](image)

According to the mineral database www.mindat.org, the value of the hardness of magnetite in mineral form is found to be around 681 HV and 792 HV. In contrast, the hardness of mild steel revolves around 100 HV and 200 HV. Therefore, the magnetite coating should increase the surface hardness of the steel specimens.
Fig. 4.3.2 shows the penetration against load curve of the mild steel specimen during loading and unloading. It can be seen that six indentations were made on the surface of the steel with an average depth of 1.4 μm. As a result of the load-penetration curve analysis, the indentation hardness of the mild steel specimen is found to be around 150 HV. Hence, the hardness value found in the microhardness test concurs with the value provided by the supplier (149 HV).

In addition, the loading and unloading curves shown in the Fig. 4.3.2 follows the indentation behaviour characteristic of ductile material. As a result, the indented surface undergoes plastic deformation and did not recover its original thickness upon unloading. The high percentage of plastic deformation (92.99%) measured in the test further supports this observation.
Fig. 4.3.3, on the other hand, shows the result of the microhardness test done on a specimen blackened in a 25% nitrate blackening bath at 150 °C and for 45 minutes. As seen in Fig. 4.3.3, the average penetration depth of the indenter is around 1.2 μm, which is less than that of the steel specimen. It can also be seen that the microhardness of the specimen increases from around 150 HV for the steel specimen to around 164 HV for the blackened specimen. This is due to the fact that magnetite has a greater hardness value than mild steel, hence the higher combined hardness of the blackened steel.

In contrast with the steel specimen, the blackened specimen experienced a mix between elastic and plastic deformation. The magnetite coating, being a brittle material, only undergo elastic deformation, whereas the underlying steel contributes to the plastic deformation of the indented surface. This is proven by the lower percentage of plastic deformation experienced by the indented surface of the specimen (87.23%).
4.4. Pin-on-disk test

Fig. 4.4.1 shows the change in the value of the friction coefficient of the bare steel specimen with the number of revolutions of the 6 mm tungsten carbide ball used in the test. The coefficient of friction of the specimen starts with a high value of 0.41. The coefficient of friction later descends to a value of 0.31, then rises back up. In general, the average coefficient of friction of the steel specimen is about 0.36.

![Friction Graph]

*Fig. 4.4.1 The coefficient of friction of the steel specimen measured in the pin-on-disk test*
It can be observed in Fig. 4.4.2 that, contrary to Fig. 4.4.1, the coefficient of friction of the specimen blackened in the 50 % nitrate bath at 140 °C for 30 minutes averaged out at a value of 0.189. This confirms that the magnetite coating has a lower coefficient of friction that the steel. In addition, it can also be seen that the value of the coefficient of friction of the magnetite coating fluctuated until the running distance reaches 2000 revolutions, whereby it stabilizes to the mean value.

![Graph showing friction values](image)

*Fig. 4.4.2 The coefficient of friction of the specimen blackened in the 50 % nitrate bath at 140 °C for 30 minutes, measured in the pin-on-disk test*
Fig. 4.4.3, on the other hand, demonstrates the coefficient of friction of the specimen blackened in the 50 % nitrate bath at 140 °C for 45 minutes. It can be seen that the coefficient of friction of the specimen is higher than that of Fig. 4.4.2, nonetheless the value is less than that of the steel specimen. Furthermore, it can be observed that the specimen has a relatively low initial coefficient of friction (0.195). However, as the running distance increases, the coefficient of friction increases up to a maximum of 0.442 and then decreases to a stable value of 0.37.

**Fig. 4.4.3** The coefficient of friction of the specimen blackened in the 50 % nitrate bath at 140 °C for 15 minutes, measured in the *pin-on-disk test*
A similar pattern is observed in the graph of the coefficient of friction of the specimen blackened in the 50 % nitrate bath at 140 °C for 45 minutes. It can be seen in Fig. 4.4.4 that the coefficient of friction increases from 0.267 up to a maximum of 0.425. The coefficient of friction then decreases until it stabilises at a value of 0.355 after 800 revolutions.

![Graph of coefficient of friction](image)

**Fig. 4.4.4** The coefficient of friction of the specimen blackened in the 50 % nitrate bath at 140 °C for 45 minutes, measured in the *pin-on-disk* test.
The variation of the coefficient of friction with the running distance of the specimen blackened in the 50 % nitrate bath at 130 °C for 30 minutes is shown in Fig. 4.4.5. As can be seen in Fig. 4.4.5, the coefficient of friction undergoes an initial transitory regime before it stabilises at an average value of 0.320.

![Friction graph](image)

**Fig. 4.4.5** The coefficient of friction of the specimen blackened in the 50 % nitrate bath at 130 °C for 30 minutes, measured in the pin-on-disk test
In continuation, the coefficient of friction of the specimen blackened in the 50 % nitrate bath at 150 °C for 30 minutes is analysed. As can be seen in Fig. 4.4.6, the coefficient of friction undergoes an initial transitory regime before it stabilises at an average value of 0.395. The transitory regime for this specimen is seen distinctive to the other specimens, in that it takes up a longer running distance than the others.

![Friction vs Running Distance Graph]

**Fig. 4.4.6** The coefficient of friction of the specimen blackened in the 50 % nitrate bath at 150 °C for 30 minutes, measured in the pin-on-disk test
The specimen blackened in the 10 % nitrate bath at 140 °C for 30 minutes has a starting coefficient of friction of 0.252, as seen in Fig. 4.4.7. As the running distance increases, the coefficient of friction also increases up to a maximum of 0.608. After about 1200 revolutions, the coefficient friction then decreases to a steady value of about 0.47.

![Friction graph](image)

**Fig. 4.4.7** The coefficient of friction of the specimen blackened in the 10 % nitrate bath at 140 °C for 30 minutes, measured in the pin-on-disk test
The highest value of the coefficient of friction is obtained for the specimen blackened in the 25% nitrate bath at 140 °C for 15 minutes. As can be observed in Fig. 4.4.8, the mean coefficient of friction of the specimen is about 0.517. With respect to the trend in the change of the coefficient of friction with the running distance, it can be seen that the coefficient of friction increases from 0.429 to a maximum of 0.550. After approximately 2000 revolutions, the coefficient of friction then follows a downward trend.

Fig. 4.4.8 The coefficient of friction of the specimen blackened in the 25% nitrate bath at 140 °C for 15 minutes, measured in the pin-on-disk test.
The coefficient of friction of the specimen blackened in 100 % nitrate bath at 140 °C for 30 minutes is demonstrated in Fig. 4.4.9. It can be appreciated that the pattern of the variation of the coefficient of friction is quite analogous to that of the steel specimen. Moreover, the average value of the coefficient of friction (0.348) also closely follows that of the steel specimen (0.363), albeit a little lower. The explanation behind this behaviour is that thickness of the magnetite coating in this case is relatively low compared to the other specimens (2 μm), thus the magnetite coating is scraped off earlier on in the pin-on-disk test. As a result, the coefficient of friction of the underlying steel substrate was measured instead of the magnetite.

**Fig. 4.4.9** The coefficient of friction of the specimen blackened in the 100 % nitrate bath at 140 °C for 30 minutes, measured in the pin-on-disk test

In conclusion, the coefficient of friction of the magnetite coating ranges between 0.189 and 0.517. This concurs with the observation in [6], which states that the coefficient of friction of the magnetite coating is between 0.40 and 0.56.
4.5. Wear analysis

As the tungsten carbide ball slides across the specimen's surface during the pin-on-disk test, it removes some of the material on the surface and generates a circular wear canal on the specimen. A section of the wear canal on the specimen blackened in the 50% nitrate at 150 °C and for 30 minutes are shown in Fig. 4.5.1. Abrasion marks, parallel to the sliding direction, can be clearly observed on the wear canal. In addition, greyish patches of material different from that of the magnetite coating can also be detected on the wear canal.

![Fig. 4.5.1 The SEM micrograph of the wear canal on the surface of the blackened specimen and the EDS spectrum of the of the black material on the wear canal.](image)

An analysis of the composition of the material on the wear canal was also done using Electron Dispersion Spectroscopy (EDS). As can be seen in the EDS spectrum in Fig. 4.5.1, the region where the abrasion marks were found on the wear canal consists of iron and oxygen atoms. Further quantitative analysis reveals that the iron atoms constitute 38.98% of the material in the region, while the remaining 61.02% is made up of oxygen atoms. Thus, the empirical formula of the material is that of red rust, Fe₂O₃, which might have been generated by the oxidation of the magnetite coating due to the friction heating during the pin-on-disk test.

Fig. 4.5.2, on the other hand, shows the EDS analysis of the grey material on the wear canal. As shown in Fig. 4.5.2, the EDS spectrum obtained shows the existence of tungsten peaks, besides the iron and oxygen peaks which signals the presence of magnetite and red rust. The tungsten peaks can be explained by the adhesion of tungsten carbide molecules to the magnetite surface.
The wear tracks generated on the surface of the specimens by the pin-on-disk test were analysed so as to determine their specific wear rate. As seen in Fig. 4.5.3, the tungsten carbide ball managed to carve out a wear track with an area of about 270 μm² and a depth of 1 μm on the steel surface. It can also be observed that the surface is fairly smooth due to prior grinding.
On the contrary, as shown in Fig. 4.5.4, the area of the wear track produced on the blackened steel specimen was determined to be about 66.1 μm². The specimen shown in Fig. 4.5.4 was blackened in the 50 % nitrate concentration bath, at a temperature of 130 °C and for a dwell time of 30 minutes. Hence, it can be seen that the wear experienced by the blackened specimen is less than that experienced by the steel specimen.

**Fig. 4.5.4** The profile of the surface of the specimen blackened in the 50 % nitrate bath at 140 °C for 30 minutes, showing the wear canal highlighted in red

Fig. 4.5.5 shows the surface profile obtained by the Form TalySurf measuring instrument of the specimen blackened in the 50 % nitrate bath at 140 °C for 15 minutes. It can be observed that the wear track on the surface has an area of 168 μm². It can also be seen that the depth of the wear track reaches a value of around 1 μm, which is less than the measured thickness of the magnetite coating. This ensures that the wear rate measured is that of the magnetite coating and not that of the underlying steel substrate.

**Fig. 4.5.5** The profile of the surface of the specimen blackened in the 50 % nitrate bath at 140 °C for 15 minutes, showing the wear canal highlighted in red
In continuation, the wear track on the surface of the specimen blackened in the 50 % nitrate bath at 140 °C for 45 minutes was analysed, as demonstrated in Fig. 4.5.6. It can be seen that the wear canal has an area of 94.2 μm² and a depth of about 0.88 μm. Consequently, the specimen experienced a relatively low value of wear compared to the previous specimens.

![Graph showing profile of specimen surface with wear canal highlighted in red.](image)

**Fig. 4.5.6** The profile of the surface of the specimen blackened in the 50 % nitrate bath at 140 °C for 45 minutes, showing the wear canal highlighted in red

Fig. 4.5.7 shows the wear track on the surface of the specimen blackened in the 50 % nitrate bath at 130 °C for 30 minutes. As seen in Fig. 4.5.7, the wear track generated on the surface is 1.05 μm deep and has an area of 119 μm². Furthermore, the wear track is seen to be very jagged which is probably due to the rough surface finish of the tungsten carbide ball.

![Graph showing profile of specimen surface with wear canal highlighted in red.](image)

**Fig. 4.5.7** The profile of the surface of the specimen blackened in the 50 % nitrate bath at 130 °C for 30 minutes, showing the wear canal highlighted in red

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Similar to Fig. 4.5.7, the wear track on Fig. 4.5.8 is also quite shallow and jagged in appearance. As seen in Fig. 4.5.8, the wear track on the surface of the specimen blackened in the 50% nitrate bath at 150 °C for 30 minutes has an area of 92.2 μm². The wear track, being shallow with a depth of 0.88 μm, is found within the boundary of the magnetite coating.

As seen in Fig. 4.5.9, the specimen blackened in the 10% nitrate bath at 140 °C for 30 minutes has a wear track with an area close to that of Fig. 4.5.8. The surface finish of the specimen is seen to be quite rough, probably due to insufficient grinding.
The wear track on the surface of the specimen blackened in the 25 % nitrate bath at 140 °C for 15 minutes is exhibited in Fig. 4.5.10. The wear track appears to be quite wide in comparison with the wear tracks on the other blackened specimens. Moreover, the wear track also possesses an area of 155 μm², which is the biggest thus far. Hence, this specimen experienced the greatest wear compared to the other blackened specimens.

Fig. 4.5.10 The profile of the surface of the specimen blackened in the 25 % nitrate bath at 140 °C for 15 minutes, showing the wear canal highlighted in red

The specimen blackened in the 100 % nitrate bath at 140 °C for 30 minutes, in contrast, has the smoothest surface and the deepest wear track compared to the other blackened specimens. This is demonstrated in Fig. 4.5.11, where the wear track is found to be 2.24 μm deep and has an area of 122 μm². In terms of area of the wear track, it is the second biggest, with the biggest being that of Fig. 4.5.10.

Fig. 4.5.11 The profile of the surface of the specimen blackened in the 100 % nitrate bath at 140 °C for 30 minutes, showing the wear canal highlighted in red
In continuation, the variation of the wear rate with the dwell time, temperature and the nitrate concentration were plotted to determine their respective effect on the wear rate of the magnetite coating. Fig. 4.5.12 displays the effect of the dwell time on the wear rate. It can be seen that the specific wear rate is the least for the specimen blackened for 30 minutes (0.0137 mm$^3$/m$\times$N), whereas the specific wear rate is the highest for a dwell time of 15 minutes (0.0309 mm$^3$/m$\times$N). Moreover, the specific wear rate follows a descending trend as the dwell time increases.

Fig. 4.5.12 The variation of the specific wear rate of the magnetite coating with the dwell time, with the temperature set at 140 °C and the nitrate concentration at 50 %.

As the magnetite coating grows in the blackening solution, the coating becomes denser and the pores on the magnetite coating become blocked [7]. As a result, the magnetite coating becomes more resistant to wear the longer it sits in the blackening bath, as is observed in Fig. 4.5.12.
Similar to Fig. 4.5.12, the specific wear rate of the magnetite coating also decreases with increasing bath temperature, as seen in Fig. 4.5.13. Regarding the value of the specific wear rate, the specific wear rate is lowest for the specimen blackened at 140 °C (0.0137 mm$^3$/m$^\cdot$N), while the specific wear rate is highest for the specimen blackened at 130 °C (0.0258 mm$^3$/m$^\cdot$N).

![Graph: Specific wear rate vs. Temperature](image)

_**Fig. 4.5.13** The variation of the specific wear rate of the magnetite coating, with the bath temperature, with the nitrate concentration set at 50% and the dwell time at 30 minutes._

The possible explanation behind this observation is that, at higher temperatures, the oxidation reaction rate increases, causing the magnetite coating to grow faster. Hence, the specimen blackened at 150 °C has a denser magnetite coating after 30 minutes compared to the specimens blackened at 140 °C and 130 °C. As mentioned before, a denser magnetite coating contributes to an improvement of the wear resistance property of the magnetite coating.
Nitrate concentration, on the other hand, doesn’t seem to affect the wear resistance of the magnetite coating. As shown in Fig. 4.5.14, the specific wear rate for the blackened specimens is seen to be fluctuating about an average value of 0.02 mm$^3$/m•N. It can also be observed that the specific wear rate of the blackened specimens has a range between 0.014 mm$^3$/m•N and 0.032 mm$^3$/m•N.

![Graph](image)

**Fig. 4.5.14** The variation of the specific wear rate of the magnetite coating with the nitrate concentration, with the temperature set at 140 °C and the dwell time at 30 minutes.

A possible explanation behind the similar specific wear rate among the blackened specimens at different nitrate concentrations is that the magnetite coatings produced in different nitrate concentration, but at the same temperature and dwell time, have the same microstructure and adherence to the steel substrate. A globular magnetite structure [6] produced via the direct oxidation mechanism was formed on the surface of the blackened specimen at a temperature of 140 °C and a dwell time at 30 minutes regardless of the nitrate concentration. This globular magnetite structure in turn gives the coating a good wear resistance property.

In conclusion, the specific wear rate of the magnetite coating (0.022 mm$^3$/m•N) is generally 50 % lower than that of the steel substrate (0.048 mm$^3$/m•N). Therefore, the magnetite coating provides a wear resistant coating over the steel substrate. Furthermore, the wear resistance property of the magnetite coating is increased at higher bath temperature and longer dwell time. The nitrate concentration, however, does not contribute to the improvement of the wear resistance property of the magnetite coating.
4.6. Electrochemical corrosion test

The traditional function of a blackening process is to provide a corrosion resistant coating on steel surfaces. Hence, the magnetite coating obtained in the blackening experiments should demonstrate a higher corrosion resistance than the bare steel specimen.

Fig. 4.6.1 demonstrates the potentiodynamic polarization plot for the steel specimen, showing the anodic and cathodic curves of the plot. It can be seen that the steel specimen has a corrosion potential value, $E_{\text{corr}}$, of -0.95 V and a corrosion current density value, $I_{\text{corr}}$, of 0.002 μA. In addition, it can also be noticed that the plot is symmetrical about the corrosion potential.

![Potentiodynamic Polarization Plot](image)

*Fig. 4.6.1 The potentiodynamic polarization plot (blue graph), adjusted to a Tafel plot (red graph) for the steel specimen.*
In comparison, the corrosion potential for a specimen blackened in the 10 % nitrate bath at 140 °C for 15 minutes is about -2.8 V, as seen in Fig. 4.6.2. The corrosion potential for the blackened specimen is thus more cathodic than that of the steel specimen. Furthermore, the specimen has a corrosion current density of $1 \cdot 10^{-6}$ μA, much lower than that of the steel specimen. This means that the corrosion rate of the blackened specimen is much smaller than that of the steel specimen. Therefore, the magnetite film in the specimen provides a passivating coating over the steel substrate.

Fig. 4.6.2 The potentiodynamic polarization plot (blue graph), adjusted to a Tafel plot (red graph) for the specimen blackened in the 10% nitrate bath at 140 °C for 15 minutes.
Similar to Fig. 4.6.2, the specimen blackened in the 100% nitrate bath at 140 °C for 15 minutes has a symmetrical polarization plot as can be seen in Fig. 4.6.3. Nonetheless, the corrosion potential of the specimen (-1.64 V) is higher than that of the specimen blackened in the 10% nitrate bath. Besides, the specimen has the lowest corrosion current density ($9.46 \times 10^{-16} \mu A$) compared to the other blackened specimens. In other words, the specimen has the best corrosion resistance among the blackened specimen.

Fig. 4.6.3 The potentiodynamic polarization plot (blue graph), adjusted to a Tafel plot (red graph) for the specimen blackened in the 100% nitrate bath at 140 °C for 15 minutes.
On the contrary, as can be observed in Fig. 4.6.4, the specimen blackened in the 10% nitrate bath at 130 °C for 15 minutes has an asymmetric plot, with a more pronounced anodic portion than the cathodic portion. It can be observed that the initial current density present on the surface of the specimen is appreciably high compared to the previous specimens. Nevertheless, the corrosion potential of the specimen (-1.29 V) is still less than that of the steel specimen (-0.97 V). The corrosion current density, however, is quite high (5.78 μA).

**Fig. 4.6.4** The potentiodynamic polarization plot (blue graph), adjusted to a Tafel plot (red graph) for the specimen blackened in the 10% nitrate bath at 130 °C for 15 minutes.
As can be seen in Fig. 4.6.5, the shape of the polarization plot of the specimen blackened in the 10% nitrate bath at 150 °C for 15 minutes is analogous to that of Fig. 4.6.4. Furthermore, the value of the corrosion potential of the specimen (-1.26 V) also closely follows that of the specimen blackened at 130 °C. Contrary to the previous specimens, the corrosion current density of the specimen at 236.39 μA is notably high.

**Fig. 4.6.5** The potentiodynamic polarization plot (blue graph), adjusted to a Tafel plot (red graph) for the specimen blackened in the 10% nitrate bath at 150 °C for 15 minutes.
A similar pattern is observed in the plot of the specimen blackened in the 10% nitrate bath at 150 °C for 30 minutes in Fig. 4.6.6. Moreover, the specimen has a corrosion potential of -1.25 V and a corrosion current density of 321.3 μA, which closely resembles that of the specimen blackened for 15 minutes. It is possible that the similar thickness of both specimens (3.1 μm) is the reason behind the similarity in the corrosion resistance of the two specimens.

Fig. 4.6.6 The potentiodynamic polarization plot (blue graph), adjusted to a Tafel plot (red graph) for the specimen blackened in the 10% nitrate bath at 150 °C for 30 minutes.
A peculiar change to the previous pattern is observed in Fig. 4.6.7, which shows the potentiodynamic polarization plot of the specimen blackened in the 10% nitrate bath at 150 °C for 45 minutes. It can be seen that the anodic and the cathodic portions of the polarization plot is symmetrical. In addition, the specimen has a corrosion potential of -0.74 V and a corrosion current density of 0.019 μA. Besides, it is interesting to note that the values of the corrosion potential and current density closely follows that of the steel specimen.

![Graph showing potentiodynamic polarization plot and Tafel plot](image)

**Fig. 4.6.7** The potentiodynamic polarization plot (blue graph), adjusted to a Tafel plot (red graph) for the specimen blackened in the 10% nitrate bath at 150 °C for 45 minutes.
Next, the variation of the corrosion potential with the dwell time and the bath temperature is analysed. Fig. 4.6.8 demonstrates the change of the corrosion potential, \( E_{\text{corr}} \), of the blackened specimen with the dwell time in the blackening solution. It can be seen that the corrosion potential is approximately the same for the specimens blackened for 15 minutes and 30 minutes (-1.25 V). However, after 30 minutes, the corrosion potential of the blackened specimen rises to a value similar to that of the bare steel specimen. This shows that, after 30 minutes in the 10 % blackening bath, the compressive stress generated by the increasingly denser magnetite coating causes it to crack, creating new pores on the coating.

**Fig. 4.6.8** The variation in the specimen’s corrosion potential with the dwell time in the 10 % nitrate blackening bath. The specimens were blackened at a temperature of 150 °C.
The effect of the bath temperature on the corrosion resistance of the blackened specimen were analysed in Fig. 4.6.9. It is observed that the specimen blackened at 140 °C has the lowest corrosion potential, whereas the specimen blackened at 130 °C and 150 °C has a higher corrosion potential. The explanation behind this observation is that the specimen blackened at 140 °C has a dense, low porosity magnetite coating, whereas the other two specimens have a more porous coating. As the oxidation rate is higher at higher bath temperature, the magnetite coating becomes denser and less porous when the temperature increases from 130 °C to 140 °C. However, as the temperature increases to 150 °C, the compressive stress generated by the increasingly denser magnetite coating causes it to crack, producing new pores on the coating.

![Graph](image)

*Fig. 4.6.9 The variation in the specimen’s corrosion potential with the temperature in the 10 % nitrate blackening bath. The specimens were blackened for 30 minutes.*

To sum up, the blackened steel generally possesses a lower corrosion potential that that of the bare steel, hence the corrosion resistance of the specimen improves with the presence of the magnetite coating. In addition, the best corrosion resistance is obtained for the specimen blackened in the 10 % nitrate bath, at a temperature of 140 °C and for 15 minutes. Furthermore, the dwell time and the bath temperature affects the corrosion resistance by changing the porosity of the magnetite coating.
5. DISCUSSION

The thickness of the magnetite coating is thought to play a pivotal role in determining its wear resistance and corrosion resistance. Henceforth, the relationship between the coating thickness and the corresponding properties is discussed in the following paragraphs.

Fig. 5.1 shows the relationship between the specimen’s mass loss and the magnetite coating thickness. An inverse relationship was found between the thickness of the magnetite coating and the mass loss of the specimen, as shown in Fig. 5.1. This observation demonstrates the fact that as the magnetite coating grows, more of the iron atoms on the steel surface is dissolved into the solution and the iron atoms were replaced by lighter oxygen atoms in the magnetite coating.

![Graph showing the relationship between thickness (μm) and mass change (%).](image)

*Fig. 5.1 The relationship between the mass change after the blackening process and the thickness of the magnetite coating*
Upon finishing the mechanical and corrosion tests on the specimens, the magnetite coating on the specimens were stripped off using a 32 % hydrochloric acid solution. The mass difference between the specimen before and after the stripping process was calculated to determine the mass of the magnetite coating. Fig. 5.2 demonstrates the relationship between the thickness of the magnetite coating with the coating mass. It can be observed that the coating mass increases as the coating thickness increases, which indicates that the density of the coating is uniform.

*Fig. 5.2 The relationship between the magnetite coating mass and the thickness of the magnetite coating*
In continuation, Fig. 5.3 demonstrates the relation between the thickness of the magnetite coating and the specific wear rate of the coating. As shown in Fig. 5.3, the specific wear rate of the magnetite coating decreases with increasing coating thickness. Hence, this proves that the wear resistance of the specimen is improved with increasing magnetite coating thickness.

![Graph showing the relation between thickness and specific wear rate](image)

**Fig. 5.3** *The relation between the thickness of the magnetite coating and the specific wear rate of the coating.*
On the other hand, the corrosion resistance of the specimen reduces with thicker magnetite coating. Fig. 5.4 demonstrates this fact by showing the anodic shift of the corrosion potential with greater coating thickness. As the corrosion potential becomes more positive, the specimen becomes more prone towards the formation of rust, Fe₂O₃. Consequently, a thicker magnetite coating provides less protection for the steel substrate against corrosion.

![Graph](image)

**Fig. 5.4** The relation between the thickness of the magnetite coating and the corrosion potential, $E_{\text{corr}}$, of the coating.

The explanation behind this counterintuitive behaviour of the magnetite coating is that as the coating becomes thicker, it also becomes more porous. The porosity of the magnetite coating is due to the increased compressive stress caused by the increase in density of the magnetite coating, which creates new pores on the coating.

A mechanism of magnetite thin film growth on the steel substrate is proposed to explain the findings in this study. In this mechanism, the iron atoms on the specimen’s surface are dissolved during the early period of the blackening process, oxidized to form magnetite particles and precipitated back on the surface of the specimen. In addition, the steel surface also experiences direct oxidation by the reactants in the blackening solution.

As the magnetite coating grows, the initially porous coating becomes denser up to the point that the pores are all closed up. At this point, the dissolution of the iron atoms and the direct oxidation of the steel surface are inhibited. However, the precipitation of magnetite particles from the blackening solution onto the specimen’s surface continues, further increasing the density of the magnetite coating. The increased compressive stress in the coating due to the increased magnetite density finally causes the coating to crack, producing new pores on the coating.
6. CONCLUSIONS

Magnetite coating of an average thickness of 3 μm was successfully obtained using the hot alkaline blackening process. In addition, the thickest coating was obtained when the specimen is blackened in 25% nitrate bath at 140 °C and for 30 minutes (5.77 μm).

A mechanism of magnetite thin film formation is proposed in this study. The mechanism consists of the formation of magnetite nuclei through the direct oxidation route and the growth of the magnetite film through the precipitation route. The initial magnetite film is initially porous, but the increase in the density of the magnetite film closes the pores. However, further increase in density produces excessive compressive stress in the coating, creating new pores on the coating.

As a result of the characterization of the magnetite coating, it was found that the presence of the magnetite coating improves the wear resistance of the steel specimens. The specimen with the best wear resistance is that of the specimen blackened in 50 % nitrate bath at 140 °C and for 30 minutes with a specific wear rate of 0.0137 mm³/m·N, which is less than half that of the steel substrate (0.048 mm³/m·N).

In addition, the corrosion resistance of the specimens are also improved by the presence of the magnetite coating. The best corrosion protection is provided by the magnetite coating produced on the specimen blackened in 10 % nitrate bath at 140 °C and for 15 minutes, which has a corrosion potential of -2.9 V, which is more cathodic than that of the bare steel (-0.98 V).

In conclusion, the best magnetite coating is obtained at a bath temperature of 140 °C with a dwell time between 15 minutes and 30 minutes. In addition, the nitrate concentration of the bath should be between 25 % and 50 % to produce magnetite coating of good quality.
## 7. BUDGET

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8. ACKNOWLEDGMENT

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